Supporting Information: Preferential Ion Adsorption in Blue Energy Applications

Christopher Balzer,[†,¶] Leying Qing,[‡,¶] and Zhen-Gang Wang[*,†]

†*Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 E California Blvd, Pasadena, California 91125, USA*

‡*State Key Laboratory of Chemical Engineering and School of Chemical Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China*

¶*These authors contributed equally.*

E-mail: zgw@caltech.edu

Contents

List of Figures

1 Description of CDLE Process

Figure S1a shows the four states of the CDLE process involving two open and two closed circuits during the charging/discharging process. The corresponding thermodynamic cycle is shown in Figure S1b. The charging process takes the system from state I to state II. In state I, the external circuit is closed and the porous electrodes are surrounded by saltwater. The cell is charged from Q_s^L to Q_s^H, which has a corresponding adsorption of charged counterions to the electrode surfaces. The surface voltage increases from ΔV_s^L to the potential difference ΔV (also called the "base voltage" and "external voltage" in the limit of infinite charging time). From state II to III, the external circuit is opened and the saltwater is replaced with the freshwater. In this process, the surface charge density remains fixed because the circuit is open, and the surface voltage difference increases to a higher surface voltage, ΔV_s^H. The surface voltage increases due to the inverse relation between the electrostatic potential difference and the ion concentration of the solution.[S1] In state III, the two porous electrodes are surrounded by freshwater. After closing the external circuit, the surface charge density gradually decreases from Q_s^H to Q_s^L, and the corresponding surface voltage difference from ΔV_s^H to ΔV, resulting in a reverse current in the closed circuit. In state IV, the circuit is opened again, and the freshwater is replaced with the saltwater. The surface voltage difference decreases from ΔV to ΔV_s^L with a surface charge density Q_s^L.

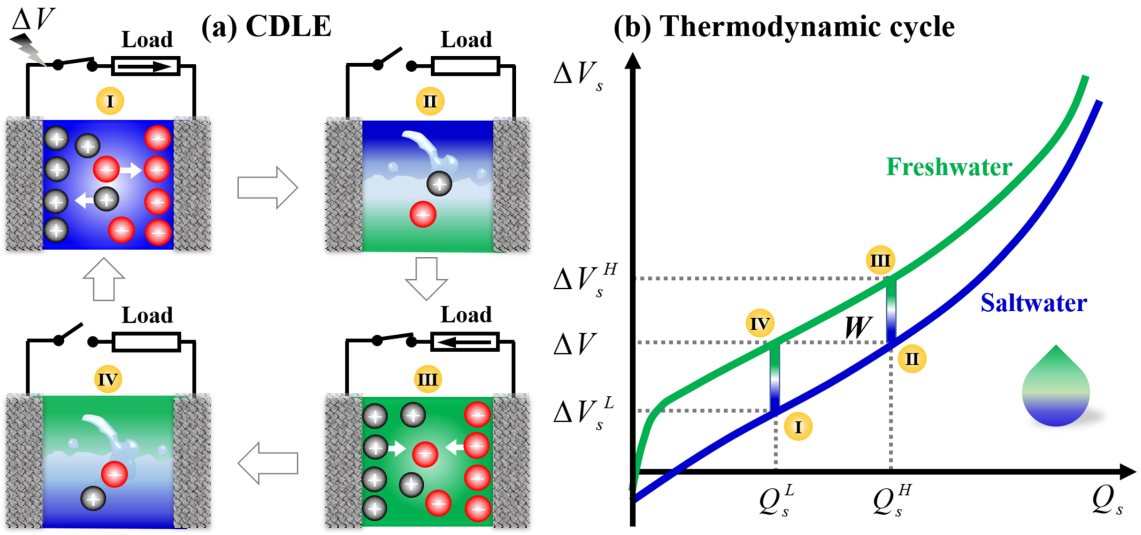

Figure S1: (a) Schematic representation of the four states in CDLE process including two open-circuit and two closed-circuit states. (b) Thermodynamic cycle in the CDLE process. ΔV_s is the applied surface voltage difference between the positive and negative electrodes in the capacitor. Q_s is the surface charge density of the electrodes. Same as Figure 1 in the main text. Reproduced here for completeness.

2 Classical Density Functional Theory for Electrolyte System

In an inhomogeneous and open system with fixed chemical potential, system temperature, and volume, the grand potential is minimized at the equilibrium state,[S2]

$$\frac{\delta\Omega[\{\rho_i(\mathbf{r})\}]}{\delta\rho_i(\mathbf{r})} = 0, \tag{1}$$

In general, the grand potential is expressed as a functional of the local density profiles of species, $\Omega[\{\rho_i(\mathbf{r})\}]$.

$$\Omega[\{\rho_i(\mathbf{r})\}] = F[\{\rho_i(\mathbf{r})\}] + \sum_i \int d\mathbf{r}\rho_i(\mathbf{r})[V_i^{ext}(\mathbf{r}) - \mu_i], \tag{2}$$

where μ_i is the chemical potential of species, i, and determined by the thermodynamic condition of bulk system. $V_i^{ext}(\mathbf{r})$ is the external potential. The key quantity in the grand

potential is the intrinsic Helmholtz free energy, $F[\{\rho_i(\mathbf{r})\}]$, which is separated into two contributions: the ideal gas part $F^{id}[\{\rho_i(\mathbf{r})\}]$ and the excess term due to the intermolecular interaction $F^{ex}[\{\rho_i(\mathbf{r})\}]$.

$$F[\{\rho_i(\mathbf{r})\}] = F^{id}[\{\rho_i(\mathbf{r})\}] + F^{ex}[\{\rho_i(\mathbf{r})\}] \tag{3}$$

The ideal gas term is

$$\beta F^{id}[\{\rho_i(\mathbf{r})\}] = \sum_i \int d\mathbf{r}\rho_i(\mathbf{r})\{\ln[\rho_i(\mathbf{r})\Lambda_i^3] - 1\}, \tag{4}$$

and taking derivative of the ideal gas free energy with respect to the density, we obtain the ideal chemical potential

$$\mu_i^{id}(\mathbf{r}) = \ln[\rho_i(\mathbf{r})\Lambda_i^3] \tag{5}$$

Combining Eqs. (1), (2), (3) and (5), the density profiles of ion species have

$$\rho_i(\mathbf{r}) = \frac{1}{\Lambda_i^3} \exp\left[\beta\left(\mu_i - V_i^{ext}(\mathbf{r}) - \frac{\delta F^{ex}[\{\rho_i(\mathbf{r})\}]}{\delta\rho_i(\mathbf{r})}\right)\right] \tag{6}$$

The excess free energy $F^{ex}[\{\rho_i(\mathbf{r})\}]$ captures additional physical effects by accounting for any intermolecular interactions beyond the ideal gas. For the electrochemical system, three contributions are included: the hard-sphere repulsions (also call excluded volume effect or steric effect), $F^{hs}[\{\rho_i(\mathbf{r})\}]$, the electrostatic correlation contribution, $F^{el}[\{\rho_i(\mathbf{r})\}]$, and the direct coulomb interaction, $F^{c}[\{\rho_i(\mathbf{r})\}]$.

$$F^{ex}[\{\rho_i(\mathbf{r})\}] = F^{hs}[\{\rho_i(\mathbf{r})\}] + F^{el}[\{\rho_i(\mathbf{r})\}] + F^{c}[\{\rho_i(\mathbf{r})\}] \tag{7}$$

In Eq. (7), the first term is obtained by the modified fundamental measure theory (MFMT) extended by Yu and Wu,[S3] according to the original FMT proposed by Rosenfeld.[S4]

$$\beta F^{hs}[\rho(\mathbf{r})] = \int \Phi^{hs}[n_\alpha(\mathbf{r})]d\mathbf{r}, \tag{8}$$

where Φ^{hs} is the reduced excess Helmholtz energy density, and depends on six weighted densities, $n_\alpha(\mathbf{r})$.[S5]

$$\Phi^{hs} = -n_0\ln(1-n_3) + \frac{n_1 n_2 - \mathbf{n}_{V_1}.\mathbf{n}_{V_2}}{1-n_3} + \frac{n_2^3 - 3n_2\mathbf{n}_{V_2}\cdot\mathbf{n}_{V_2}}{36\pi}\left[\frac{\ln(1-n_3)}{n_3^2} + \frac{1}{n_3(1-n_3)^2}\right] \tag{9}$$

where six weighted densities $n_0(\mathbf{r})$, $n_1(\mathbf{r})$, $n_2(\mathbf{r})$, $n_3(\mathbf{r})$, $\mathbf{n}_{V_1}(\mathbf{r})$, and $\mathbf{n}_{V_2}(\mathbf{r})$ are related to the weight functions $\omega_i^{(\alpha)}(\mathbf{r})$, $\alpha = 0,\ 1,\ 2,\ 3,\ V_1,\ V_2$.

$$n_\alpha(\mathbf{r}) = \sum_i n_{\alpha,i}(\mathbf{r}) = \sum_i \int \rho_i(\mathbf{r}')\omega_i^{(\alpha)}(\mathbf{r}-\mathbf{r}')d\mathbf{r}' \tag{10}$$

The weight functions is employed to describe the geometry of the hard-sphere particle, mainly including two scalar functions associated with the volume and surface area, and a surface vector function.

$$\omega_i^{(3)}(\mathbf{r}) = \theta(\sigma_i/2 - |\mathbf{r}|) \tag{11}$$

$$\omega_i^{(2)}(\mathbf{r}) = \delta(\sigma_i/2 - |\mathbf{r}|) \tag{12}$$

$$\omega_i^{(V_2)}(\mathbf{r}) = \frac{\mathbf{r}}{|\mathbf{r}|}\delta(\sigma_i/2 - |\mathbf{r}|) \tag{13}$$

Another three weight functions are

$$\omega_i^{(1)}(\mathbf{r}) = \omega_i^{(2)}(\mathbf{r})/(2\pi\sigma_i) \tag{14}$$

$$\omega_i^{(0)}(\mathbf{r}) = \omega_i^{(2)}(\mathbf{r})/(\pi\sigma_i^2) \tag{15}$$

$$\omega_i^{(V_1)}(\mathbf{r}) = \omega_i^{(V_2)}(\mathbf{r})/(2\pi\sigma_i) \tag{16}$$

$\theta(\mathbf{r})$ is the Heaviside step function, and $\delta(\mathbf{r})$ is the Dirac delta function. In Eq.(7), the second term because of the electrostatic correlation is obtained by a quadratic functional Taylor expansion with respect to the bulk density of ions by neglecting the higher-order correlations.

$$\begin{aligned}\beta F^{el}[\{\rho_i(\mathbf{r})\}] =& \beta F^{el}[\{{\rho_i}^b\}] + \sum_i \int d\mathbf{r}\Delta C_i^{(1)el}[\rho_i(\mathbf{r}) - {\rho_i}^b] \\ &- \frac{1}{2}\sum_{i,j}\int\int d\mathbf{r}d\mathbf{r}'\Delta C_{ij}^{(2)el}(|\mathbf{r}-\mathbf{r}'|) \times [\rho_i(\mathbf{r}) - {\rho_i}^b] \times [\rho_j(\mathbf{r}') - {\rho_j}^b]\end{aligned} \tag{17}$$

where ${\rho_j}^b$ is the bulk density of ions. $\Delta C_i^{(1)el}$ and $\Delta C_i^{(2)el}$ represent one-order and two-order direct correlation functions, respectively.

$$\Delta C_i^{(1)el} = -\frac{\delta\beta F^{el}}{\delta\rho_i(\mathbf{r})}\bigg|_b \tag{18}$$

$$\Delta C_{ij}^{(2)el}(|\mathbf{r}-\mathbf{r}'|) = -\frac{\delta^2\beta F^{el}}{\delta\rho_i(\mathbf{r})\delta\rho_j(\mathbf{r}')}\bigg|_b \tag{19}$$

The one-order DCF is clearly proportional to the excess chemical potential in the bulk fluid; the two-order DCF can be expressed as

$$\Delta C_{ij}^{(2)el}(r) = C_{ij}(r) - C_{ij}^{hs}(r) - C_{ij}^{c}(r) \tag{20}$$

where $C_{ij}^c(r) = -l_B Z_i Z_j/r$ is the direct Coulomb correlation. The two-body DCF can be obtained from the mean-spherical approximation (MSA).[S6,S7] For $0 \le r \le |\sigma_i - \sigma_j|/2$,

$$C_{ij}(r) - C_{ij}^{hs}(r) = -2l_B[-Z_i N_j + X_i(N_i + \Gamma X_i) - \frac{\sigma_i}{3}(N_i + \Gamma X_i)^2] \tag{21}$$

and for $|\sigma_i - \sigma_j|/2 \leq r \leq (\sigma_i + \sigma_j)/2$,

$$rC_{ij}(r) - rC_{ij}^{hs}(r) = l_B[(\sigma_i - \sigma_j)L_1 - rL_2 + r^2 L_3 + r^4 L_4] \tag{22}$$

where

$$L_1 = \frac{X_i + X_j}{4}(S_i - S_j) - \frac{\sigma_i - \sigma_j}{16}[(S_i + S_j)^2 - 4N_i N_j] \tag{23}$$

$$L_2 = (X_i - X_j)(N_i - N_j) + (X_i^2 + X_j^2)\Gamma + (\sigma_i + \sigma_j)N_i N_j - \frac{\sigma_i S_i^2 + \sigma_j S_j^2}{3} \tag{24}$$

$$L_3 = \frac{X_i}{\sigma_i}S_i + \frac{X_j}{\sigma_j}S_j + N_i N_j - \frac{S_i^2 + S_j^2}{2} \tag{25}$$

$$L_4 = \frac{S_i^2}{6\sigma_i^2} + \frac{S_j^2}{6\sigma_j^2} \tag{26}$$

The parameters used in here have $S_i = N_i + \Gamma X_i$, $\Gamma = \sqrt{\pi l_B \sum_i \rho_i^b X_i^2}$, and $N_i = \frac{X_i - Z_i}{\sigma_i}$. In addition, X_i can be solved through the following two equations:

$$(1 + \Gamma\sigma_i)X_i + \nu\sigma_i^2 \sum_j \rho_j^b \sigma_j X_j = Z_i \tag{27}$$

$$\nu \equiv (\pi/2)\left[1 - (\pi/6)\sum_i \rho_i^b \sigma_i^3\right]^{-1} \tag{28}$$

Then, we have

$$X_i = \frac{Z_i}{1 + \Gamma\sigma_i} - \frac{\nu\sigma_i^2}{1 + \Gamma\sigma_i}\left[\sum_j \frac{\rho_j^b \sigma_j Z_j}{1 + \Gamma\sigma_j} \Big/ \left(1 + \nu\sum_j \frac{\rho_j^b \sigma_j^3}{1 + \Gamma\sigma_j}\right)\right] \tag{29}$$

In Eq. (7), the last term from the direct coulomb interaction has

$$F^c[\{\rho_i(\mathbf{r})\}] = \sum_i \psi(\mathbf{r}) Z_i e \rho_i(\mathbf{r}) - \frac{\epsilon_0 \epsilon_r}{2}[\nabla\psi(\mathbf{r})]^2 \tag{30}$$

where $\psi(\mathbf{r})$ is the average electrostatic potential. In general, $\psi(\mathbf{r})$ can be solved by Poisson equation.

3 Trends in Spontaneous Voltage

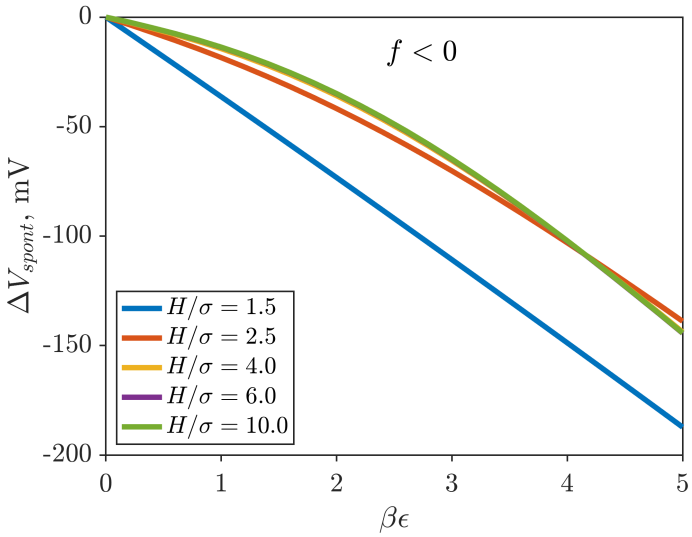

Figure S2: Spontaneous voltage for $f < 0$ and a variety of pore sizes and preferential adsorption strengths. The concentration of saltwater is 0.6 M.

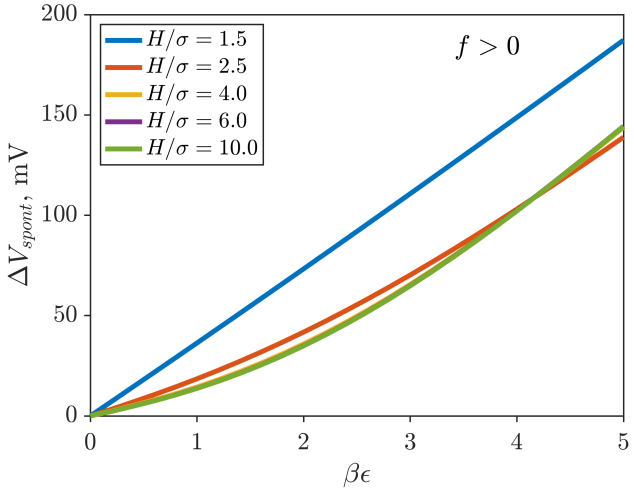

Figure S3: Spontaneous voltage for $f > 0$ and a variety of pore sizes and preferential adsorption strengths. The concentration of saltwater is 0.6 M. The lines for $H/\sigma = 6$ and $H/\sigma = 10$ overlap.

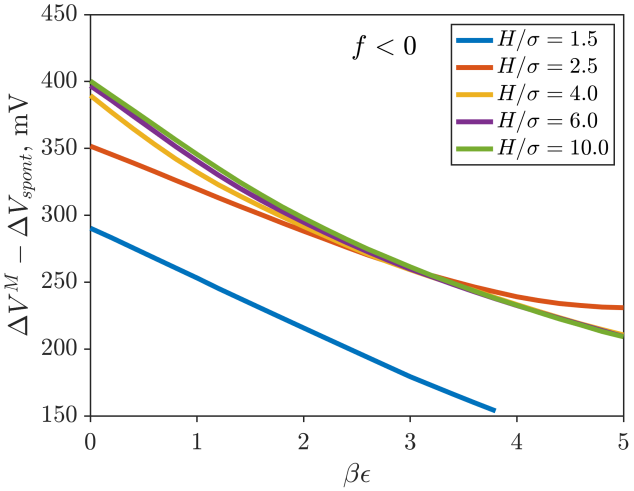

Figure S4: Difference between the potential difference of maximum energy and the spontaneous voltage for $f < 0$ and a variety of pore sizes and preferential adsorption strengths. The concentration of freshwater is 0.024 M, and the concentration of saltwater is 0.6 M.

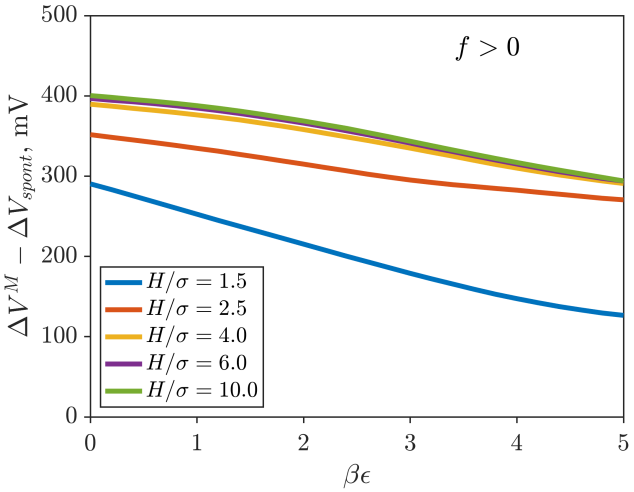

Figure S5: Difference between the potential difference of maximum energy and the spontaneous voltage for $f > 0$ and a variety of pore sizes and preferential adsorption strengths. The concentration of freshwater is 0.024 M, and the concentration of saltwater is 0.6 M.

4 Maximum Energy per Volume of Electrolyte

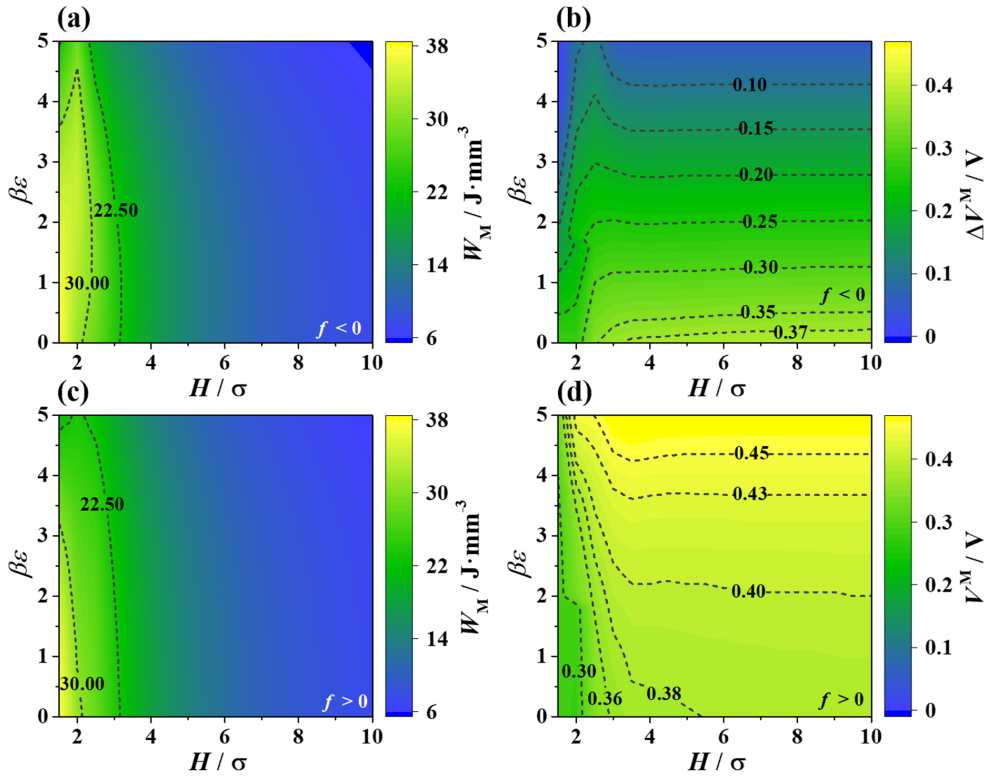

Figure S6: Heat map of (a) the maximum available energy W_M per volume of electrolyte and (b) the corresponding potential difference ΔV^M in the plane of $\beta\epsilon$ and H/σ for $f < 0$. Panels (c-d) are identical to (a-b) with $f > 0$. The concentration of freshwater is 0.024 M, and the concentration of saltwater is 0.6 M.

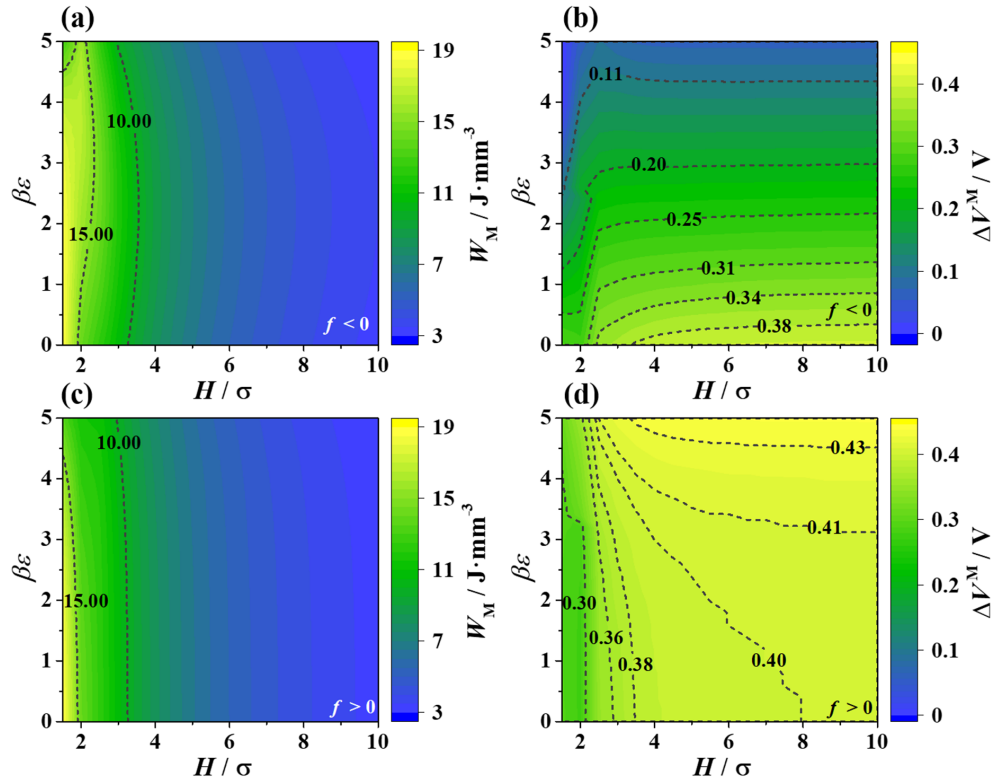

Figure S7: Heat map of (a) the maximum available energy W_M per volume of electrolyte and (b) the corresponding potential difference ΔV^M in the plane of $\beta\epsilon$ and H/σ for $f < 0$. Panels (c-d) are identical to (a-b) with $f > 0$. The concentration of freshwater is 0.024 M, and the concentration of saltwater is 2.0 M.

References

(S1) Brogioli, D. Extracting renewable energy from a salinity difference using a capacitor. *Physical Review Letters* **2009**, *103*, 058501, DOI 10.1103/PhysRevLett.103.058501.

(S2) Hansen, J.-P.; McDonald, I. R. *Theory of simple liquids*; Elsevier, 1990; Chapter 3, pp 46–57.

(S3) Yu, Y.-X.; Wu, J. Structures of hard-sphere fluids from a modified fundamental-measure theory. *The Journal of Chemical Physics* **2002**, *117*, 10156–10164, DOI 10.1063/1.1520530.

(S4) Rosenfeld, Y. Structure and effective interactions in multi-component hard-sphere liq-

uids: the fundamental-measure density functional approach. *Journal of Physics: Condensed Matter* **2002**, *14*, 9141–9152, DOI 10.1088/0953-8984/14/40/308.

(S5) Li, Z.; Wu, J. Density-functional theory for the structures and thermodynamic properties of highly asymmetric electrolyte and neutral component mixtures. *Physical Review E* **2004**, *70*, 031109, DOI 10.1103/PhysRevE.70.031109.

(S6) Blum, L. Mean spherical model for asymmetric electrolytes: I. Method of solution. *Molecular Physics* **1975**, *30*, 1529–1535, DOI 10.1080/00268977500103051.

(S7) Hiroike, K. Supplement to Blum's theory for asymmetric electrolytes. *Molecular Physics* **1977**, *33*, 1195–1198, DOI 10.1080/00268977700101011.